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QUANTITATIVE ANALYSIS OR RARE EARTHS BY X-RAY FLUORESCENCE SPECTROMETRY

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ABSTRACT

Rare earths ores and compounds are of growing importance to the worldwide industry. Its applications range from raw material to catalysts, manufacturing of electronics and even supermagnets. Therefore, the demand for quick and accurate quantitative analysis methods is continuously growing.
Current quantification methods of rare earths involve the separation of these elements by ion exchange and liquid-liquid extraction prior to the analysis itself, processes both time and reagent consuming.
In the present work, we propose a method that directly quantifies by XRF technique the following rare earths: La, Pr, Nd, Sm and Gd in a concentrated liquor whose matrix also contains Ca, Y, PO4, U and Th.
We evaluated the analytical interference of each element present on the sample on X-rays spectrum. The studied samples are certified standards and the obtained results have been compared to EDTA titration results, an already well-stablished and widely trusted method.We also measured the matrix effect thus using a complex rare earths standard. Results show that quantification by XRF technique is as accurate as the results in dose titration with EDTA for the same elements, with the advantage of exempting the previous separation step from each rare earth and from other elements present in the matrix (such as U and Th).

1. INTRODUCTION

The rare earth elements (REEs) include lanthanides (atomic number between 57 and 71) and yttrium, which has a chemical behaviour similar to the heavier lanthanides. REEs are generally divided into light (from La to Sm) and heavy (from Eu to Lu) REEs. They present similar chemical and physical properties.

Many of the existing classical methods for the determination of REEs have been superseded by physical techniques, including spectroscopic techniques. Atomic
absorption and plasma emission spectrometry have recently been used for the simultaneous determination of lanthanides at lower concentrations [1].

However, apart from plasma spectrometry, these methods were not satisfactory. For concentrations greater than 1 $mg.g^{-1}$, X-ray fluorescence (XRF) spectrometry is probably still the most versatile technique.

The big advantage for the use of XRF analysis in REEs is the ability of quantifying each individual element without provided separation in columns.
The matrix effect can be suppressed by the standard addition technique in calibration curves for each element.

Some studies using wavelength dispersion X-ray fluorescence - WDXRF for quantification of REEs have been performed obtaining satisfactory results for relatively low concentrations such as 0,002 ng ml^{-1} Y and Gd [2].

However, quantitative methods using Particle Induced X-Ray Emission (PIXE) for quantification of REEs did not show good results for concentrations at the ng ml^{-1}[3].
Some studies have shown that it is possible to analyze concentrations less than 10 ng ml^{-1} of REEs in samples pretreated by concentration with a complex of activated carbon and then subjected to energy dispersion X-ray fluorescence (EDXRF) [4].

Here we present results obtained in a liquid matrix containing La, Ce, Pr, Nd, Sm, Gd and Y ($g.L^{-1}$) containing U and Th which still held the quantification of individual REE by EDXRF technique without previous separation among them.

2. EXPERIMENTAL

2.1. Instrumentation

The characteristics and operating conditions of the equipment EDXRF are described in Table.

Table 1: X-Ray Fluorescence Spectrometer with Energy Dispersive (EDXRF) parameters

Model Number	EDX 800HS
Brand	Shimadzu
Detector	Si (Li)
Conditions	Automatic analysis for Qualitative / Quantitative Ti to U.
Used Atmosphere	Air
X-ray tube	Rh with 50KV and 1000μA
collimator	10mm

2.2. Chemicals

We used the following reagents and materials: Lanthanium oxide, Cerium oxide, Neodymium oxide, Samarium oxide, Gadolinium oxide, Yttrium oxide and Uranium oxide (Johnson Matthey Chemicals Limited), Praseodymium oxide (SPEX – Industries, INC.), Thorium nitrate, EDTA and methylene blue (Merck), hydrochloric acid (Isofar), 2.27 $mg.cm^{-2}$ filter paper disc with 0.9 mm Ø(J.PROLAB), film with 55 µm thickness (Mylar™).

2.3. Analytical procedure

All solutions were prepared from analytical-reagent grade. Tri-distilled water was used in all dilutions. Thorium, Uranium and REEs solutions were obtained by dissolving their salt or oxide with hydrochloric acid (Isofar). The solutions were standardized with EDTA and methylene blue. Series of 5 solutions were prepared with increasing concentrations for each REEs from their stock solutions.The final concentration for each stock solutions (in HCl 2.5 $molL^{-1}$ medium) and the concentration of series prepared are shown in Table 2. The solutions were pipetted (20µl) on paper disks with 9mm of diameter. It was dried in lamp and covered with film to measurement by EDXRF.

In order to analyze the effect matrix and the influence of U and Th in the quantification of individual REEs a solution containing the same concentration of all REEs study was prepared (STANDARD MIX - SM). The concentration of each element in SM is shown in Table 3. Calibration curves were made for each individual element in the study.

A Standard Mix scan was performed aimed to study which analytical lines of each element would be suitable for quantification, in other words, one that does not suffer influence of another element present in the sample. Still using SM, calibration curves were made for each individual element where a known quantity of the SM was added to each point in order to prove the possibility of quantifying each element despite the effect caused by the complex matrix.

Table 2: Standard Solutions Concentration

ANALYTE	STOCK SOLUTION	SOLUTION 1	SOLUTION 2	SOLUTION 3	SOLUTION 4	SOLUTION 5
Y	17.4752	3.5765	6.9583	10.4598	13.8846	17.4751
La	16.2450	2.9941	6.5173	9.9724	12.9690	16.2450
Ce	13.2585	2.9790	5.4439	7.9160	10.4752	13.2585
Pr	18.2285	4.5279	7.4326	10.4598	13.8846	18.2284
Nd	16.0961	3.0330	6.4223	9.9722	12.9090	16.0961
Sm	15.5283	2.9815	6.0003	8.9899	12.5027	15.5283
Gd	18.6807	3.9843	7.5292	11.5171	14.9553	18.6807
Th	13.1531	2.9716	5.4897	8.5187	10.9679	13.1531
U	14.5645	3.0479	5.9799	8.9994	11.9592	14.5645

**The associated uncertainty is ± 0.0001 for each value.*

***The concentration were obtained by EDTA titration method and described in $g.L^{-1}$*

Table 3: Mix Standard Concentration

ANALYTE	CONCENTRATION	ANALYTE	CONCENTRATION
Y	0.0075± 0.0001	Sm	0.0075± 0.0001
La	0.0075± 0.0001	Gd	0.0075± 0.0001
Ce	0.0075± 0.0001	Th	8.5187± 0.0001
Pr	0.0075± 0.0001	U	8.9994± 0.0001
Nd	0.0075± 0.0001		

**The concentration of the solutions is described in $g.L^{-1}$*

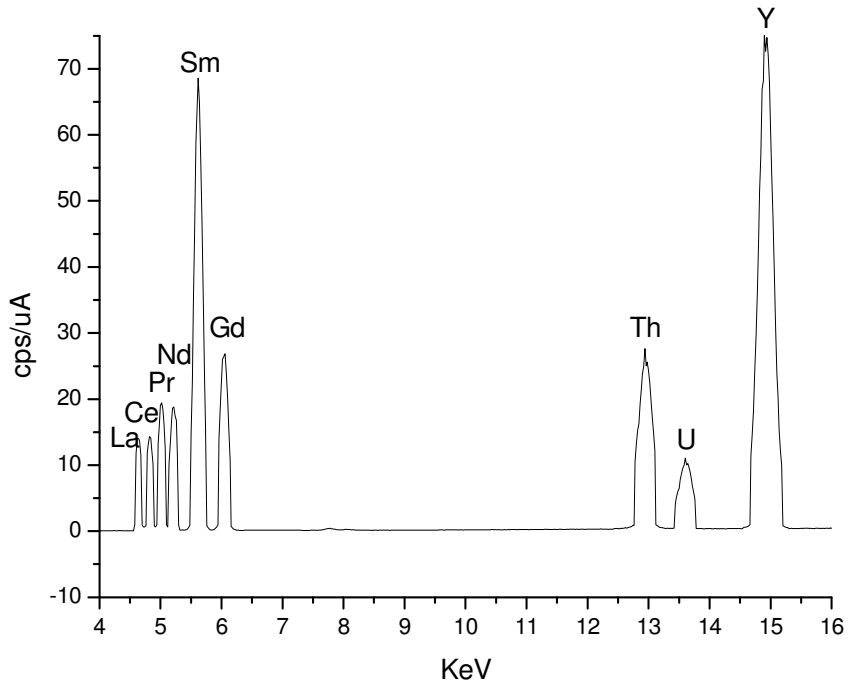
3. RESULTS AND DISCUSSION

3.1. Qualitative Evaluation of REEs Standard Mix

The scan spectrum shown in Figure 1 demonstrates the peaks of each element in the Standard Mix at the energy line Lα1.

The other analytical lines were suppressed in the analysis by EDXRF, considering that were some coincidences among the various elements analyzed.
The signals obtained at Lα1 showed good intensity at studied concentrations - ranging between 2.9716 $g.L^{-1}$ and 18.6807 $g.L^{-1}$ ±0.0001 - for all REEs.

Figure 1: Scan of Mix Standart by EDXRF



3.2. Quantitative analysis of REEs

In order to measure the signal in Lα1 a selective quantitative analysis was performed in EDXRF equipment. The measures are given in the solutions 1, 2, 3, 4 and 5 of each series of elements, starting with Y and ending with the U. The results were analyzed by linear regression graph (Figure 2) and their respective equations and coefficients are listed in Table 4.

Calibration curves were evaluated in pure matrix without interference.

The signals obtained - as well as the linear equations presented - show that the technique for quantifying REEs by EDXRF in pure solutions has good reproducibility and accuracy.

Figure 2: Calibration curves of REEs by EDXRF

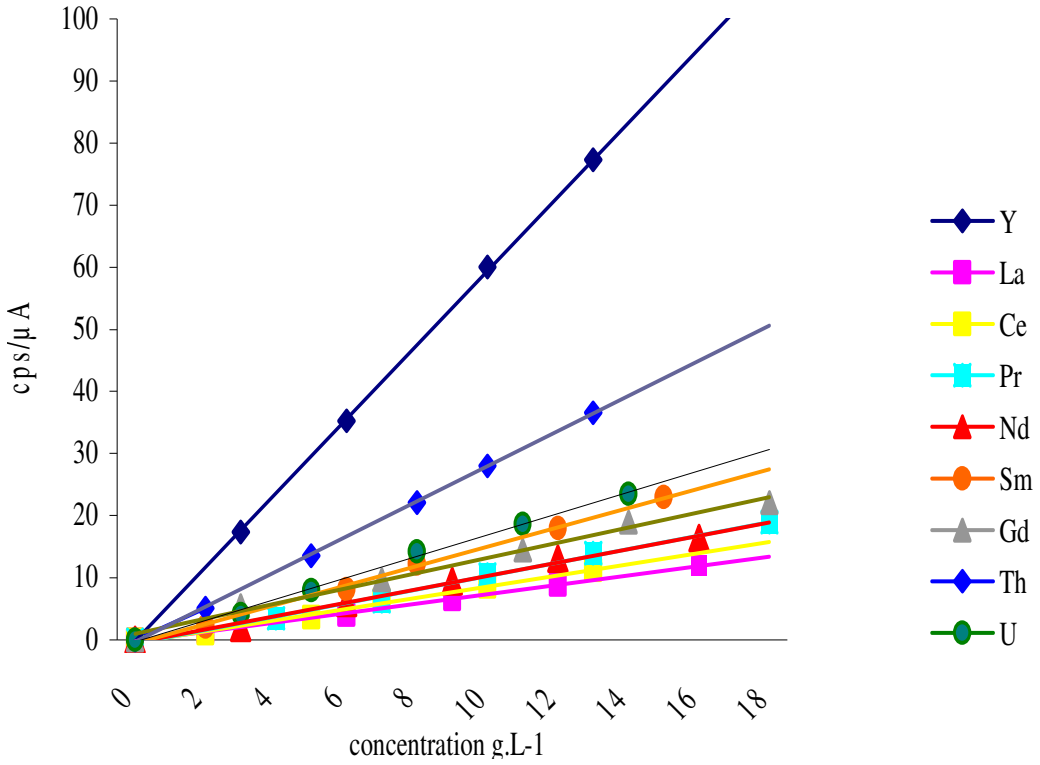


Table 4: Linear equation of the standard addition curves of REEs

REE	Linear equation	Correlation coefficient
Y	Ycps = (5.964[Y] ± 0.001) –(0.2205±0.001)	0.9999
La	La cps = (0.2783[La] ± 0.001) - (0.3372± 0.002)	0.9965
Ce	Ce cps = (0.3232[Ce] ± 0.001) - (0.0904± 0.008)	0.9989
Pr	Pr cps = (0.4210[Pr] ± 0.001) - (0.6436± 0.001)	0.9981
Nd	Nd cps = (0.4208[Nd] ± 0.001) – (0,4914± 0.002)	0,9996
Sm	Sm cps = (0,5967 [Sm] ± 0.001) - (0,4363± 0.001)	0,9992
Gd	Gd cps = (0,4980 [Gd] ± 0.001) + (0,1550± 0.003)	0,9965
Th	Th cps = (2,8299[Th] ± 0.001) - (0,3584± 0.001)	0,9997
U	U cps = (0,6450[U] ± 0.001) – (0,5216± 0.002)	0,9997

**Results are expressed as mean ± standard deviation (n = 5).*

3.3. Quantitative analysis of REEs

The standard addition curves for each REEs were performed at constant concentration of Standard Mix (SM). The signals were measured in the analytical line Lα1. Table 5 shows the signals and values of REEs concentration obtained in each point at the respective curves.

After linear regression, the linear equation shows the calculated value for the concentration of each element in the Standard Mix (first point of each curve) as shown in Figure 3.

The results in Table 6 show that the effect caused by complex matrix (SM) containing REEs and also U and Th does not hinder the quantification of the REEs by EDXRF technique. The calculated values for the concentration of each element analyzed in SM are very close to the real concentration of these elements in SM.

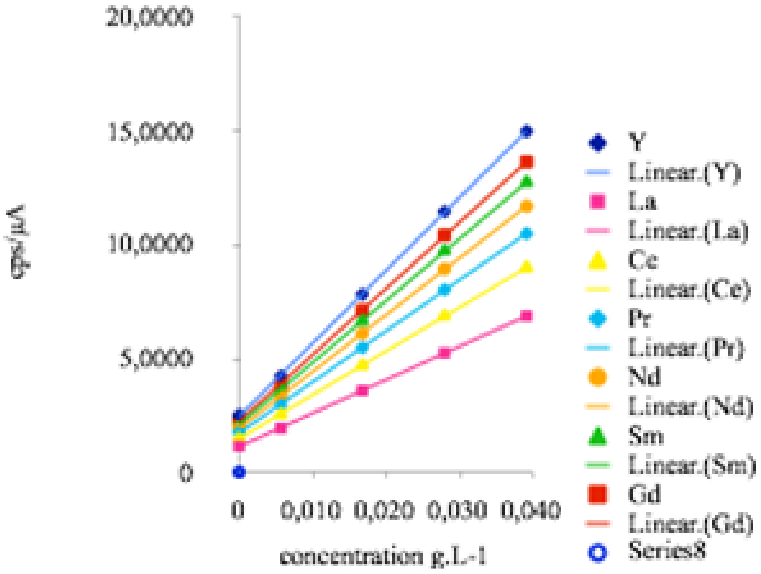


Figure 3: Standard addition curves by EDXRF

Table 5: Numerical results of standard addition REEs

[REEs]	Y cps/µA	La cps/µA	Ce cps/µA	Pr cps/µA	Nd cps/µA	Sm cps/µA	Gd cps/µA
0.0000	2.5103	1.1497	1.5061	1.7572	1.9580	2.1337	2.2843
0.0057	4.2336	1.9389	2.5401	2.9635	3.3022	3.5985	3.8525
0.0168	7.8212	3.5821	4.6927	5.4748	6.1005	6.6480	7.1173
0.0280	11.4556	5.2466	6.8733	8.0189	8.9353	9.7372	10.4246
0.0392	14.9895	6.8651	8.9937	10.4926	11.6918	12.7410	13.6404

**The concentration of the solutions is described in g.L^{-1}*

Table 6: Numerical results of standard addition REEs

REE	Linear equation	Correlation coefficient	[REE] expected g.L^{-1}	[REE] observed g.L^{-1}
Y	Ycps = 319.79[Y] + 2.4651	R2 = 0.9999	0.0075	0.0076±0.0001(1.3%)
La	La cps = 146.23[La] + 1.129	R2 = 0.9999	0.0075	0.0076±0.0001(1.49%)
Ce	Ce cps = 191.37[Ce] + 1.479	R2 = 0.9999	0.0075	0.0078±0.0001(1.57%)
Pr	Pr cps = 223.15[Pr] + 1.7255	R2 = 0.9999	0.0075	0.0077±0.0002(2.83%)
Nd	Nd cps = 249.23[Nd] + 1.9228	R2 = 0.9999	0.0075	0.0077±0.0002(2.97%)
Sm	Sm cps = 272.02[Sm]+ 2.0953	R2 = 0.9999	0.0075	0.0073±0.0003(4.93%)
Gd	Gd cps= 290.91[Gd] + 2.2432	R2 = 0.9999	0.0075	0.0078±0.0002(2.11%)

*Results are expressed as mean ± standard deviation (n = 5). Coefficient of variation is between parentheses.

4. CONCLUSIONS

The Quantitation of rare earths in complex samples account great analytical difficulty because it requires a long separation and purification treatment of REEs, before quantification of each individual.

U and Th are a further obstacle to this analysis, considering that both form a complex with most reagents used in optical spectroscopy measurements of Rare Earths.

The present work has demonstrated satisfactory results for the quantification of the studied rare earths.

The main advantage is that prior separation between the analysed elements is not necessary. Another advantage is the capacity of working with liquid samples. The use of solid samples in standard addition methods can also be tested since these are fixed in an absorbent material which retains the added standard homogeneously.

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